

UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP014295

TITLE: An Approach to Nanoglasses through Anodic Oxidation of
Sputtered Aluminum on Glass Surface

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings Volume 740
Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for
Structural Applications

To order the complete compilation report, use: ADA417952

The component part is provided here to allow users access to individually authored sections
of proceedings, annals, symposia, etc. However, the component should be considered within
the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP014237 thru ADP014305

UNCLASSIFIED

An Approach to Nanoglasses through Anodic Oxidation of Sputtered Aluminum on Glass Surface

Satoru Inoue, Song-Zhu Chu, Kenji Wada

National Institute for Materials Science, Advanced Materials Laboratory,
Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

ABSTRACT

The new processes for the preparation of nanoglasses have been developed through anodic oxidation. The aluminum thin film sputtered on the ITO thin film on the glass surface was decomposed into alumina by anodic oxidation technique. The alumina layer possessed nanometer size pore array standing on the glass surface. The sizes of the pore was widened by acid etching from 10–20nm to a few hundred nm. The glass substrate having the alumina nanostructures on the surface could transmit the UV and visible light at the wavelength range of 200 ~ 800nm. The TiO_2 sol was impregnated into the pores of alumina layer and the sample was heated at ~ 400 °C for 2 hr, converted into TiO_2 nanotubes of anatase phase. The acid etching could remove the alumina skeletons, leaving the TiO_2 nanotube array on the glass surface. These glasses were transparent to the light in UV-visible region. The electro deposition technique was applied to the introduction of Ni metal into pores, giving Ni nanorod array on the glass surface. The glass samples possessing TiO_2 nanotube array showed very good catalytic function on the decomposition of acetaldehyde gas under the irradiation of UV light. The effect of the dimensions of the Ni nanorods on the magnetization was investigated.

INTRODUCTION

The anodic oxidation of aluminum has been used as the method to convert the aluminum surface into alumina for the improvement of the chemical durability. The anodic oxidation technique is known as the self organization process to generate the porous alumina where the nanopores are arranged as perpendicular to the substrate. Recently nanostructured materials have attracted great interest for their potentiality leading to the unique functions in the optical properties, electronic properties, magnetic properties and mechanical properties. In these years, the porous anodic alumina has been studied to fabricate the nanostructured materials [1~5]. The anodic oxidation of the thin aluminum film has been studied recently on the sputtered aluminum film on the Ta [6] and the Si [7] substrate, resulting in the oxidation of the aluminum layer followed by the oxidation of the substrate.

The authors have been studying the formation of the nanostructures on glass surfaces and have developed the new process in which the sputtered alumina film on the conductive layer (tin-doped indium oxide (ITO)) on the glass substrate was converted into the nanostructures by anodic oxidation [8]. The authors have also been studying the processes to introduce other compounds into nanopores of the anodic alumina using sol-gel technique and electro deposition. The TiO_2 component could be introduced by sol-gel process [9,10] giving the high efficiency photo catalytic function [11]. The density of the nanopores of the alumina nanostructures on the glass surface was estimated to be about 1000 Gbit / inch² and the introduction of the magnetic components possessing easy magnetization axis perpendicular to the substrate would be applicable to the ultra high density magnetic recording media. The introduction of Ni metal could be attained by electro deposition process and the magnetization characteristics of the Ni nanorods were investigated [12].

In this paper, the new processes approaching to the nanoglasses which might work as the high efficiency photo catalysts or the ultra high density new magnetic recording media have been reviewed.

EXPERIMENTAL DETAILS

Specimens

Pure aluminum (99.99%) was deposited on a soda-lime-silica glass substrate coated with ITO and SiO₂ protection thin film by RF sputtering technique. The size of the substrate was 20 x 100 x 1.1 mm. The thickness of the ITO film and SiO₂ film were 100 ~ 130 nm and ~ 15 nm, respectively. The sheet resistivity of the ITO film was ~ 20 ohm. The aluminum layer was deposited at the rate of ~1.5 nm/s in 2.5 cycles (0.8 μ m per cycle) under the pressure of 1.0×10^{-5} Torr to reach ~2 μ m in the thickness.

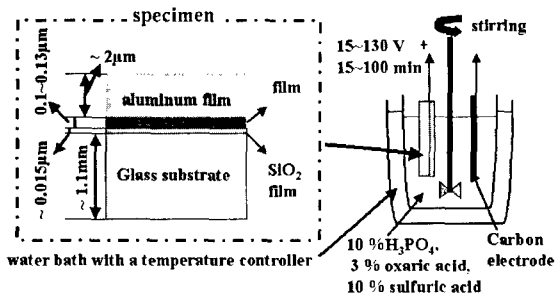


Figure 1. Setup for the anodic oxidation of aluminum film

Anodic oxidation [8]

The aluminum thin film was anodized by a regulated dc power supply in a 10 vol.% phosphoric acid solution or in a 3 % oxalic acid solution or in a 10 % sulfuric acid solution. The specimens were washed by ultrasonic-cleaning in ethanol for 10 min and were anodized in phosphoric acid at a voltage of 130 V at 280 K, in oxalic acid at 40 V at 293 K and in sulfuric acid at 15 V at 283 K. To avoid repetition, the anodic oxide films prepared in phosphoric, oxalic and sulfuric acid solutions are quoted as phosphoric films, oxalic films and sulfuric films, respectively. The setup for the anodization was shown in Figure 1. The part of the films on the substrate was enlarged and the scale of the specimen did not show the real dimensions. The anodized specimens were etched in a 5 vol.% phosphoric acid at 30°C for 2 ~ 15 min to enlarge the pore size and remove the anodic alumina barrier layers at the bottoms of the pores (to expose the ITO layer to the electrolyte) for the smooth electro deposition of Ni metal.

Sol-gel process [9,10]

The TiO₂ sol (~5 wt%) was prepared from reagent grade titanium isopropoxide, acetylacetonate, ethanol and distilled water at a mole ratio of 1:1:20:3. The reaction was carried out at room temperature in the open air. The mixture was stirred for 2 h and stored in a brown bottle at room temperature. Prior to the experiments, the sol solution was aged for 1 week ~ 1 month. Though the color of the sol changed gradually from light yellow to dark yellow, nothing precipitated and the solution was very stable.

In the introduction of TiO₂ sol into the nanopores of the anodic alumina, the specimens were first immersed in ethanol for 10 min and then dipped in the TiO₂ sol at room temperature for 20 min. After 20 min dipping, the specimens were lifted up slowly from the solution. The TiO₂ sol on the back side of the specimen was washed away with ethanol. The specimens dipped in the TiO₂ sol were dried in the air at room temperature for more than 2 h. To obtain porous alumina/titania structure, the specimens were heated in the furnace at 100°C for 1 h and at 400°C for 2 h where the heating rate was 2°C/min. To get TiO₂ nanotube array, the anodic alumina skeletons were removed with the etching by 5 % phosphoric acid and 2 % CrO₃ solution at 75°C for 5 ~ 8 min.

Electro deposition process [12]

The electrolyte solution for the Ni electro deposition consisted of 0.38 M NiSO_4 , 0.13 M NiCl_2 , 0.65 M H_3BO_3 and 60 ppm $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, and was adjusted to PH 5.2 with a 20 % NaOH solution. The specimens were immersed in distilled water for 1 min to push out the air in the pores with applying ultrasonic wave prior to the electro deposition. The Ni electro deposition was performed at 1.0 ~ 1.5 V and 30°C for 2 ~ 10 min, with stirring. The counter electrode was a pure nickel plate. To get Ni nanorods, the alumina skeletons of the specimens were removed with the etching by 5 % NaOH solution

Characterizations

The morphology of the samples were observed with a field emission scanning electron microscope (FESEM, S-500, Hitachi) with an energy-dispersion X-ray analyzer (EDXA). The thin coating of osmium was applied on the sample surfaces for the discharge during observations. The UV-visible transmission spectra were recorded by a spectrophotometer (U-3500, Hitachi). The crystalline phases were identified with an X-ray diffractometer (XRD, RINT-2000/PC, Cu Ka, 40 V / 40 mA). The transmission electron microscope (TEM, JEM-1010, 100 kV) was used to observe the structures of Ni nanorods. Magnetization curves were measured by a vibrating sample magnetometer (USM, Lake Shore model 7300). The evaluation of the photo catalysis of the TiO_2 nanotube array was performed by monitoring the volume of the CO_2 gas released in the decomposition of acetaldehyde

[11]. The popular and high performance photo catalysis, Degussa P25, was used as the reference sample. The UV light source was a 200W Hg-Xe lamp possessing the peak emission at 365nm.

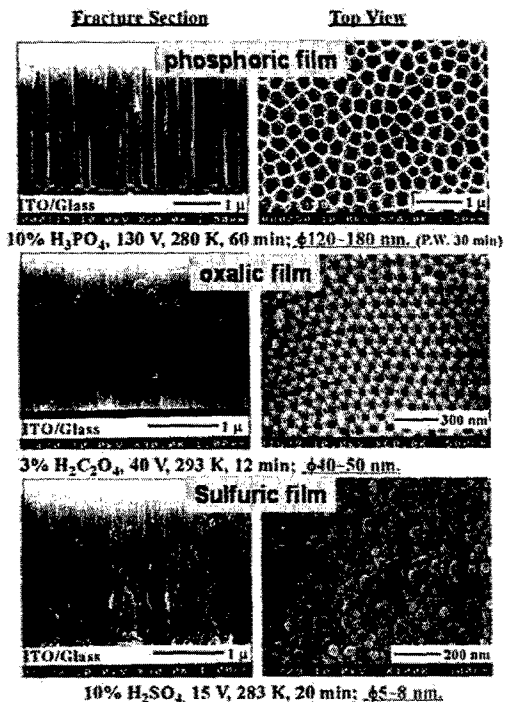


Figure 2. SEM photos of the anodic alumina on the glass surfaces.

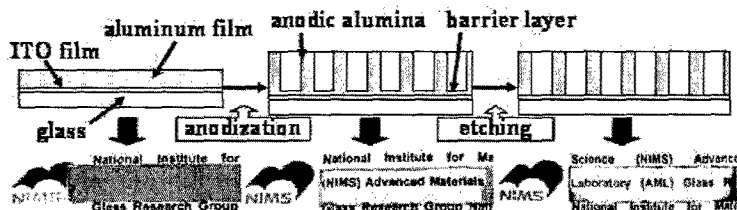


Figure 3. The photos of the specimen and the anodic alumina on the glass substrate.

RESULTS AND DISCUSSION

Nanostructures on the glass surface [8]

The FESEM photos of the anodic alumina prepared under various conditions were shown in Figure 2. The details of the preparation processes were given in the reference [12]. The pore sizes of the phosphoric film were 120 ~ 180 nm in the diameter after 30 min pore widening treatment. The pore diameters of the anodic film were 40 ~ 50 nm in the oxalic film and 5 ~ 8 nm for the sulfuric film. The pores were arranged as perpendicular to the glass substrate. The photos of the specimens were shown in Figure 3. The specimen became transparent after the anodization. The transmission spectrum of the phosphoric film was given in Figure 4 [9]. The anodic alumina film on the glass gave ~ 90 % transmission in the visible region. The waving of the spectra originated from the interference taking place within the specimen.

Introduction of TiO_2 sol into nanopores [9]

Figure 5 shows the schematic illustrations, the photos of the specimens and the SEM photos in the process for the synthesis of the TiO_2 nanotube array on the glass. After widening of the pores, the sol was introduced into pores. The SEM photo indicated that the inside wall of the pores were coated with the sol. The photo showed that the transparency was kept after the impregnation. The transmission spectrum was given in Figure 4 as " $\text{Al}_2\text{O}_3/\text{TiO}_2$ Nanostructure", showing the transmission of 30 ~ 80 % in the visible region. The specimen was converted into the TiO_2 nanotube array after dissolution of the alumina skeletons. The dimensions of the nanotubes were ~ 200 nm in the outside diameter and ~ 140 nm in the inside diameter.

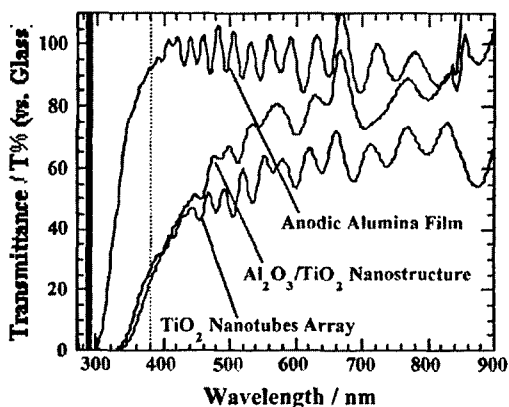


Figure 4. Transmission spectra of the nanostructures on the glass surfaces.

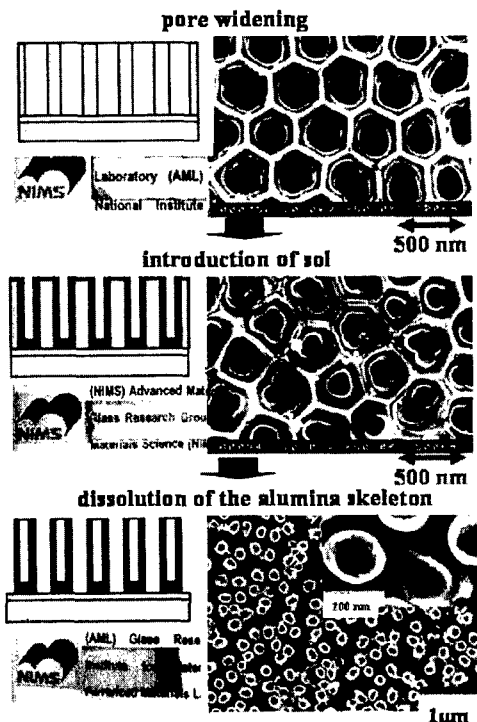


Figure 5. The synthesis of TiO_2 nanotube array.

ter. The length of the nanotubes corresponded to the thickness of the anodic alumina film and were $\sim 3 \mu\text{m}$. The translucency of the specimen was kept but the transmittance decreased a little as shown in Figure 4, where the spectrum was quoted as "TiO₂ Nanotube Array". The transmittance was $\sim 60\%$ in the visible region and decreased gradually in the UV region. The surface area of the specimen was estimated to increase by ~ 45 times from the calculation based on the simple geometry. The TiO₂ formed in the process was identified to be anatase phase by the X-ray diffraction.

Evaluation of photo catalytic function [11]

The relative value of the volume of the released CO₂ gas was plotted against the irradiation time of UV light in Figure 6. All the data were normalized to the specimen area of 1cm^2 . The impregnated anodic film on the glass gave photo catalytic function better than Degussa P25. "Porus TiO₂-P", which is the impregnated phosphoric film, showed the decomposition rate larger by ~ 13 times than that of Degussa P25. The catalytic function of the TiO₂ nanotube array has not yet been finished, but would be better for the increase of the surface area. The sulfuric film impregnated with TiO₂ sol did not seem to have open pores and was not taken in the catalytic function test.

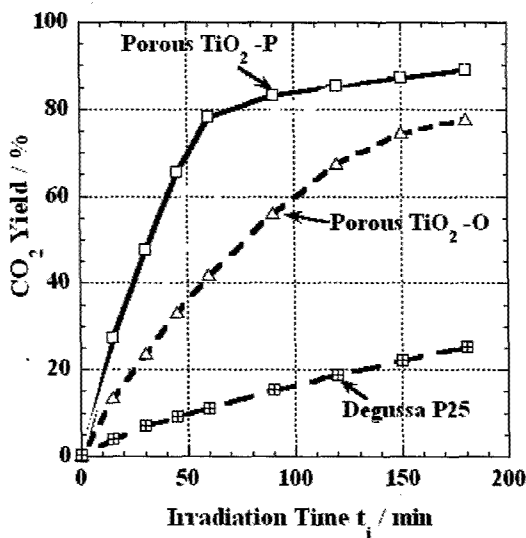


Figure 6. Evaluation of photo catalytic function.

Introduction of Ni into nanopores [12]

In Figure 7, the cross sectional SEM photos were shown for the cases of the phosphoric film and oxalic film. The Ni deposition was performed directly on the ITO film. When the anodic alumina barrier layer remained, the electro deposition could not be performed. The SEM photos of the Ni nanorod arrays, which were obtained after dissolution of anodic alumina skeletons, were summarized in Figure 8. The phosphoric film, the oxalic film and the sulfuric film gave the nanorods of $\sim 150\text{ nm}$, $\sim 50\text{ nm}$ and $\sim 18\text{ nm}$ in the diameter, respectively. The Figure 9

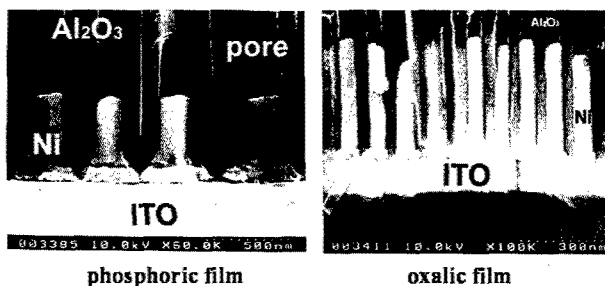


Figure 7. The cross sectional SEM photo at the interface between the Ni and ITO film. Deposition time: 2min

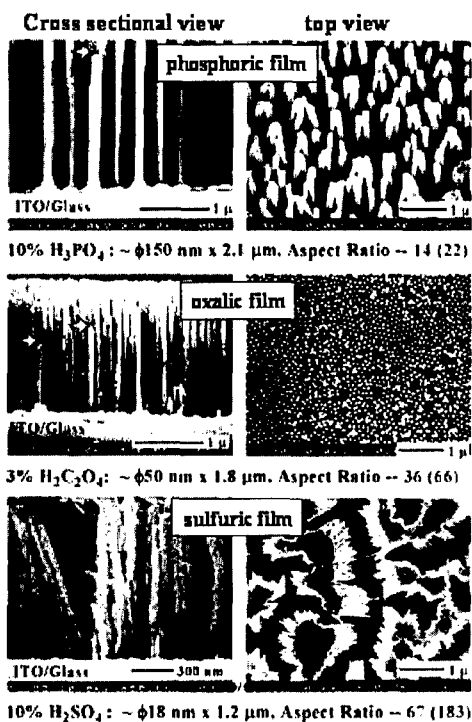


Figure 8. SEM photos of the Ni nanorod array.

shows the magnetization curves for the Ni nanorod embedded in the anodic alumina skeletons. In the figures, A.R. indicates the average aspect ratio of the Ni nanorods. The top one is for the phosphoric film, the middle one for the oxalic film and the bottom one for the sulfuric film. The figure indicated that the easy axis of magnetization changed from in-plane to perpendicular direction with the increase of the aspect ratio of the nanorod. In other words, The magnetization perpendicular to the substrate became dominant over the in-plane magnetization. Taking that the density of the pores of the anodic films were about 1000 Gbit / inch² into account, the anodic films embedded with appropriate magnetic substances could be applied to the ultra high density magnetic recording media.

CONCLUSIONS

The anodic oxidation of the sputtered alumina on the glass substrate was fruitful process to build up the nanostructures on the glass surface. The introduction of the compounds into pores could be attained with the sol-gel processing and electro deposition technique. The embedding of the components into the nanopores could endow the glasses the photo catalytic functions and would be applicable to the ultra high density magnetic recording. The photo catalyst prepared in this study showed the decomposition rate of acetaldehyde larger by an order of one than that of the Degussa P25. The anodic oxidation process, the sol-gel coating process and the electro deposition process are principally applicable to general curved substrates and large substrates. The new process does not require the special and expensive apparatuses like

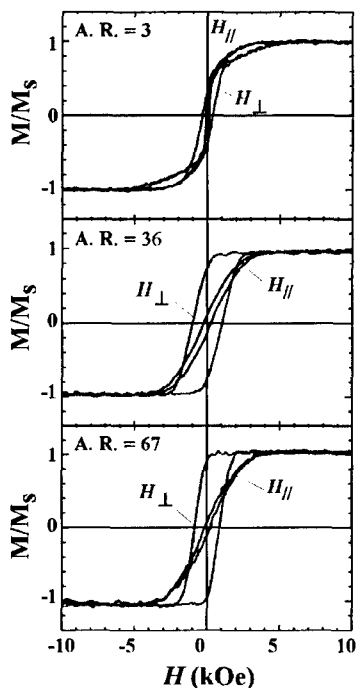


Figure 9. Magnetization curves of the Ni nanorod arrays.

high power lasers, nanometer range precise manipulators etc. Therefore the process is believed to have an advantage over the other nanomachining processes in the applications and the commercial productions.

REFERENCES

1. A. Huczko, *Appl. Phys.* **70**, 365 (2000).
2. T. Kyotani and A. Tomita, *Bull. Chem. Soc. Jpn.* **72**, 1957 (1999).
3. M. Zhang, Y. Bando, K. Wada and K. Kurashima, *J. Mater. Sci. Lett.* **18**, 1911 (1999).
4. B. B. Lakshmi, P. K. Dorhout and C. R. Martin, *Chem. Mater.* **9**, 857 (1997).
5. H. Masuda and K. Fukuda, *Science* **268**, 1466 (1995).
6. for example; A. Mozalev, A. Surganov and H. Imai, *Electrochim. Acta* **46**, 2825 (2001).
7. for example; D. Crouse, Y. Lo, A. E. Miller and M. Crouse, *Appl. Phys. Lett.* **76**, 49 (2000).
8. S. Z. Chu, K. Wada, S. Inoue and S. Todoroki, *J. Electrochem. Soc.* **149**(7), B321 (2002).
9. S. Z. Chu, K. Wada, S. Inoue and S. Todoroki, *Chem Mater.* **14**, 266 (2002).
10. S. Z. Chu, K. Wada and S. Inoue, *Advanced Materials*, **14**[23], 1752 (2002)
11. S. Z. Chu, S. Inoue, K. Wada, Di Li and H. Haneda, *J. Mater. Chem.*, (in press) (2003), also published as an Advanced Article on the RSC web site (<http://www.rsc.org/is/journals/current/jmc/mappub.htm>) on Feb. 7, 2003.
12. S. Z. Chu, K. Wada, S. Inoue and S. Todoroki, *Chem. Mater.*, **14**, 4595 (2002).